

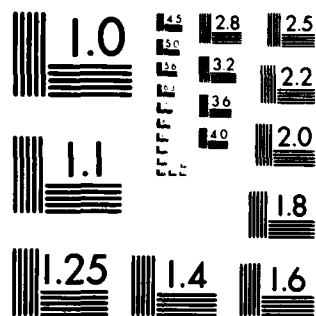
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THE CROWN ETHER PROMOTED BASE DEGRADATION OF P-CARBORANE.(U)  
APR 82 D C BUSBY, M F HAWTHORNE N00014-76-C-0390  
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The Crown Ether Promoted Base Degradation of p-Carborane

By

David C. Busby and M. Frederick Hawthorne

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# The Crown Ether Promoted Base Degradation of *p*-Carborane

By

David C. Busby and M. Frederick Hawthorne

In 1964 Wiesboeck and Hawthorne<sup>1</sup> discovered that degradation of the closo icosahedral carborane, 1,2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>, by ethanolic KOH produces a novel nido carborane anion, [7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup>, whose structure is that of an icosahedron with one vertex removed (Fig. 1). Similar treatment of 1,7-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> leads more slowly to the isomeric

## Figure 1

[7,9-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup>. In both cases, the boron atom removed is one which is adjacent to both electronegative carbon atoms which makes the boron more susceptible to nucleophilic attack. Strong base removes the bridging proton from the open face of [7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup> and [7,9-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup> to give nido-dianions which can bond to metals in a pentahapto fashion<sup>2</sup>. This discovery led to the development of the field of metallocarborane chemistry.

Attempts to degrade the third icosahedral isomer, 1,12-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>, using ethanolic KOH failed, presumably because no boron atom is adjacent to both carbons. Under more forcing conditions (20% KOH in propanediol, 170° C), Plesek and Hermanek<sup>3</sup> were able to obtain 15% yield of 2,9-C<sub>2</sub>B<sub>9</sub>H<sub>13</sub>, the protonated form of [2,9-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup>. Considering the difficulty with which the starting material, 1,12-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>, is prepared<sup>4</sup> such low yield conversions make development of the metallocarborane chemistry of the [2,9-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>2-</sup> ligand impractical; however, metallocarboranes derived from [2,9-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>2-</sup> are of particular interest because only one carbon is adjacent to the metal in contrast to [7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>2-</sup> and [7,9-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>2-</sup> derivatives.

We report here the use of a crown ether to promote a rapid, high yield degradation of 1,12-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> by KOH to give [K(18-Crown-6)][nido-2,9-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>] and the preparation of metallocarboranes derived from it.

## EXPERIMENTAL

**MATERIALS.** All solvents were reagent grade and were used without further purification. Triethylamine (MCB) was used as received, and dicyclopentadiene(MCB) was cracked to the monomer immediately prior to use. Potassium hydroxide (85%) (Mallinckrodt) was powdered under nitrogen and stored in a desiccator. The  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (Mallinckrodt) and 18-Crown-6 ether (Aldrich) were used as received and  $\text{RhCl}(\text{PPh}_3)_3$  was prepared from  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  (Johnson-Matthey) by a literature procedure<sup>5</sup>. Thermal isomerization of 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$  was used to prepare 1,12- $\text{C}_2\text{B}_{10}\text{H}_{12}$ <sup>4</sup>.

**INSTRUMENTATION.** Infrared spectra were recorded on Perkin-Elmer 137 spectrometer as KBr pellets or nujol mulls.  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were obtained on a Bruker WP-200 FTNMR spectrometer at 200.1MHz and 81.0MHz, respectively. The  $^{11}\text{B}$  NMR spectra were obtained at 126.8 MHz on a FTNMR instrument designed and constructed by Professor F.A.L. Anet of this department.  $^{11}\text{B}$  chemical shifts are referenced to external  $\text{BF}_3 \cdot \text{OEt}_2$ . Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

$[\text{K}(18\text{-Crown-6})][\text{nido-2,9-}\text{C}_2\text{B}_9\text{H}_{12}]$ . A 100 ml Schlenk flask containing an egg-shaped magnetic stirring bar was charged with 0.52 g (3.6 mmol) 1,12- $\text{C}_2\text{B}_{10}\text{H}_{12}$ , 2.12 g (32.1 mmol) powdered KOH, 4.02 g (15.2 mmol) 18-Crown-6 ether and 60 ml freshly distilled benzene. Contact time with air was minimized since both KOH and 18-Crown-6 are very hygroscopic. The flask was fitted with a condenser, flushed with argon and placed in a 100° C oil bath. The solution/suspension was magnetically stirred under positive pressure of argon for 42 h and then allowed to cool. Ethanol (5 ml) was added through the condenser and the solution stirred for 15 min. The suspension was filtered through a medium frit and the white solid washed with 10 ml 95% ethanol, 100 ml distilled water and 10 ml 95% ethanol. The remaining white solid was dissolved in 200 ml acetone, the solution filtered, mixed with 100 ml water

and the volume slowly reduced on a Buchi Rotavapor. The white crystalline product was filtered off, washed with water and a small amount of ethanol and dried briefly on the frit; yield, 1.49 g (95%). Anal. Calcd. for  $C_{14}H_{36}B_9KO_6$ : C, 38.49; H, 8.13; B, 22.27; K, 8.95. Found: C, 38.34; H, 8.29; B, 22.40; K, 9.10. IR( $cm^{-1}$ , nujol)  $\nu_{B-H}$  2520s,  $\nu_{C-O}$  1115s;  $^{11}B$  NMR ( $\delta$ , acetone) -13.10(d,  $J_{1H-11B} = 140$  Hz, 2B), -19.23(d,  $J_{1H-11B} = 148$  Hz, 2B), -21.58(d,  $J_{1H-11B} = 148$  Hz, 2B), -28.54(d,  $J_{1H-11B} = 139$  Hz, 2B), -42.94(d,  $J_{1H-11B} = 156$  Hz, 1B);  $^1H$  NMR ( $\delta$ , acetone- $d_6$ ) 3.67(s, 24 H), 2.81(s, 1H).

[NEt<sub>3</sub>H][nido-2,9-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]. A mixture of 30 ml con. H<sub>2</sub>SO<sub>4</sub>, 40 ml distilled H<sub>2</sub>O and 80 ml heptane was placed in a 250 ml Ehrlenmeyer flask equipped with a rubber septum. The mixture was cooled in an ice bath and deoxygenated with argon. The [K(18-Crown-6)][nido-2,9-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>], 0.91g (2.08 mmol) was added to the flask and the system flushed briefly with argon. Vigorous shaking led to the dissolution of the white solid. The heptane layer was decanted and the acid layer shaken with 2 X 50 ml heptane. The combined heptane portions were treated with 3 ml NEt<sub>3</sub> resulting in immediate precipitation of a white flocculent solid which was filtered off, washed with heptane and dried in vacuo overnight; yield, 0.47g (96%). Caution! The intermediate in this reaction is volatile and bad-smelling and should be handled only in a hood. IR( $cm^{-1}$ , nujol)  $\nu_{N-H}$  3060s,  $\nu_{B-H}$  2520vs;  $^{11}B$  NMR ( $\delta$ , acetone) -13.23(d,  $J_{1H-11B} = 115$  Hz, 2B), -19.19(d,  $J_{1H-11B} = 148$  Hz, 2B), -21.56(d,  $J_{1H-11B} = 145$  Hz, 2B), -28.57(d,  $J_{1H-11B} = 126$  Hz, 2B), -42.88(d,  $J_{1H-11B} = 151$  Hz, 1B).

[closo-2- $n^5$ -C<sub>5</sub>H<sub>5</sub>)-2,1,12-CoC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]. Following a procedure outlined for similar compounds by Plesek, et al.,<sup>6</sup> [K(18-Crown-6)][nido-2,9-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>], 1.72 g (3.94 mmol), KOH, 2.45 g (43.66 mmol), and 10 ml of methanol were placed in a 100 ml round-bottomed flask and swirled in an ice bath until dissolution of the KOH was complete. An additional 7 ml of methanol, 0.8 ml of freshly cracked cyclopentadiene (9.71 mmol), and 1.50 g (6.31 mmol) CoCl<sub>2</sub>·6H<sub>2</sub>O were added. The flask was fitted with a condenser, put through two freeze-pump-thaw cycles, and heated to reflux with stirring under a positive pressure of nitrogen for 6h. After cooling 50 ml of H<sub>2</sub>O was added and the

suspension filtered. The yellow-brown solid was washed with 100 ml H<sub>2</sub>O, 50 ml 10% HCl, 50 ml H<sub>2</sub>O and dried on the frit. Treatment with 50 ml benzene filtration gave a yellow filtrate which was evaporated to dryness, the solid re-dissolved in methylene chloride and eluted down a silica gel column with 1/1 methylene chloride/hexane. The eluate was evaporated to dryness to give the yellow product; yield, 0.22g (21%). IR(cm<sup>-1</sup>, Nujol)  $\nu_{B-H}$  2530s; <sup>11</sup>B NMR ( $\delta$ , CH<sub>2</sub>Cl<sub>2</sub>) -2.71

(d,  $J_{H-^{11}B}$  = 215 Hz, 1B), -4.42 (d,  $J_{H-^{11}B}$  = 164 Hz, 2B), -6.45 (d,  $J_{H-^{11}B}$  = 153 Hz, 2B), -15.55 (d,  $J_{H-^{11}B}$  = 158 Hz, 2B), -18.84 (d,  $J_{H-^{11}B}$  = 161 Hz, 2B).

[closo-2,2-(PPh<sub>3</sub>)<sub>2</sub>-2-H-2,1,12-RhC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]. Both RhCl(PPh<sub>3</sub>)<sub>3</sub>, 3.42g (3.69 mmol), and [K(18-Crown-6)][nido-2,9-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>], 1.70g (3.89 mmol), were placed in a 250 ml Schlenk flask containing a magnetic stirring bar. The flask was fitted with a condenser and the system flushed with nitrogen for 15 min. Deoxygenated ethanol (100 ml) was syringed in and the suspension heated to reflux with stirring for 1 h over which time the color of the solid changed to yellow. The flask was allowed to cool, the contents were filtered, and the yellow solid was washed with ethanol (25 ml) and heptane (25 ml) and then redissolved in methylene chloride. This solution was passed down a short silica gel column and collected in a nitrogen-flushed 500 ml Schlenk flask. The volume was reduced in vacuo to 200 ml, 100 ml heptane was added, and volume was reduced in vacuo to 75 ml. The resulting yellow crystalline solid was filtered off, washed with heptane and diethylether, and dried in vacuo; Yield, 2.72g (96%), Anal. Calcd. for C<sub>38</sub>H<sub>42</sub>B<sub>9</sub>P<sub>2</sub>Rh: C, 59.98; H, 5.56; B, 12.79; P, 8.14; Rh, 13.52. Found: C, 61.37; H, 5.36; B, 12.65; P, 8.15; Rh, 12.99. IR (cm<sup>-1</sup>, KBr)  $\nu_{C-H}$  3000w,  $\nu_{B-H}$  2530s,  $\nu_{Rh-H}$  2060w; <sup>1</sup>H NMR ( $\delta$ , CD<sub>2</sub>Cl<sub>2</sub>) -8.74 (d of tr,  $J_{^{103}Rh-^1H}$  = 15 Hz,  $^2J_{^{31}P-^1H}$  = 27 Hz; <sup>31</sup>P NMR ( $\delta$ , 10% C<sub>6</sub>D<sub>6</sub>/(THF) 34.8 (d,  $J_{^{103}Rh-^{31}P}$  = 112 Hz).



## RESULTS AND DISCUSSION

Crown ethers have long been known to enhance the nucleophilicity of anions when they are used to solubilize salts in aprotic media. For instance, Pedersen and Frensdorff used dicyclohexyl 18-Crown-6 to solubilize KOH and NaOH in benzene. The resulting solutions functioned as effective saponifying agents for substrates normally resistant to saponification. They ascribed this result to an increased dissociation of ion pairs providing highly reactive unsolvated anions<sup>7</sup>.

We have applied this method with excellent results to the basic degradation of 1,12-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>, which has previously proved to be very resistant to the standard techniques employed for the basic degradation of 1,2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> and 1,7-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>. Yields of the desired [nido-2,9-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup> of >95% were achieved in relatively short reaction times using KOH solubilized in benzene with 18-Crown-6. The exact mechanism by which the removal of the boron vertex takes place is not known at this time, but the stoichiometry we have observed clearly indicates that 4 equivalents of 18-Crown-6 are required per mole of 1,12-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>. The aprotic nature of the reaction medium is also important. The addition of only 10% ethanol to the normal benzene solvent reduces the yield to only 20% of that observed in pure benzene.

The product is isolated as a [K(18-Crown-6)] salt which is very mildly air sensitive in solution and the solid state. It is moderately soluble in acetone and acetonitrile and somewhat soluble in methylene chloride, benzene, ethanol and tetrahydrofuran. The cation may be exchanged by a two-phase acidification procedure in which the [K(18-Crown-6)] cation extracts into the water layer and the carborane intermediate, presumably 2,9-C<sub>2</sub>B<sub>9</sub>H<sub>13</sub> reported by Plesek and Hermanek<sup>3</sup>, extracts into the hydrocarbon layer. Treatment with trialkylamines gives trialkylammonium salts, [NR<sub>3</sub>H][nido-2,9-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>], in essentially quantitative yields. The cesium

salt,  $\text{Cs}[\text{nido-2,9-C}_2\text{B}_9\text{H}_{12}]$ , has also been prepared in crystalline form by neutralizing the intermediate with aqueous  $\text{CsOH}$ . The method is general with different purification methods depending upon the salt.

Based on analytical, chemical, and spectral properties, especially the symmetry indicated by the  $^{11}\text{B}$  NMR spectrum, the anion almost certainly has the structure depicted in Fig. 1; an 11-membered icosahedral fragment with the carbons in the 2 and 9 positions. This is the only thermally stable  $[\text{nido-C}_2\text{B}_9\text{H}_{12}]^-$  species known in which only of the two carbons is in the open face. Stanko, et al., have reported the preparation of  $[\text{nido-11-R-2,7-C}_2\text{B}_9\text{H}_{11}]^-$  by the low temperature alkylation of  $[\text{nido-7,8-C}_2\text{B}_9\text{H}_{11}]^{2-}$  with alkyl halides<sup>8</sup> and have confirmed the structure by X-ray crystallography<sup>9</sup>; however,  $[\text{nido-11-R-2,7-C}_2\text{B}_9\text{H}_{11}]^-$  is reported to rearrange rapidly at room temperature to give  $[\text{nido-8-R-7,9-C}_2\text{B}_9\text{H}_{11}]^-$ .

The impetus behind the preparation of  $[\text{nido-2,9-C}_2\text{B}_9\text{H}_{12}]^-$  was the desire to investigate icosahedral metallocarboranes of the form  $\text{L}_n\text{MC}_2\text{B}_9\text{H}_{11}$  in which only one carbon atom would be adjacent to the metal vertex. Two representative complexes have been synthesized using established methods. The reaction of cobaltous chloride and cyclopentadiene with  $[\text{nido-2,9-C}_2\text{B}_9\text{H}_{12}]^-$  in the presence of  $\text{KOH}$ , led to the preparation of a yellow compound which was spectroscopically identical to the material previously isolated in small quantities from the thermal isomerization of  $[\text{closo-3-(}\eta^5\text{-C}_5\text{H}_5\text{)-3,1,2-CoC}_2\text{B}_9\text{H}_{11}]$  and identified as the compound  $[\text{closo-2, (}\eta^5\text{-C}_5\text{H}_5\text{)-2,1,12-CoC}_2\text{B}_9\text{H}_{11}]$  based on  $^{11}\text{B}$  NMR and physical properties<sup>10</sup>.

Of more interest is a new rhodacarborane  $[\text{closo-2,2-(PPh}_3\text{)}_2\text{-H-2,1,12-RhC}_2\text{B}_9\text{H}_{11}]$  (I) which was synthesized from  $[\text{K(18-Crown-6)}][\text{nido-2,9-C}_2\text{B}_9\text{H}_{12}]$  and  $\text{RhCl(PPh}_3\text{)}_3$  using the method of Paxson and Hawthorne<sup>11</sup>. Details of its spectral and physical properties along with those of its isomeric analogs,  $[\text{closo-3,3-(PPh}_3\text{)}_2\text{-3-H-3,1,2-RhC}_2\text{B}_9\text{H}_{11}]$  (II) and  $[\text{closo-2,2-(PPh}_3\text{)}_2\text{-2-H-2,1,7-RhC}_2\text{B}_9\text{H}_{11}]$  (III), which have previously been reported<sup>11</sup>, will be discussed elsewhere. (I) is only mildly air-sensitive in the

solid state and in solution, decomposing over a period of time to a blue material presumably similar to the rhodacarborane dimer recently reported by Hawthorne, et al,<sup>12</sup>. Like (II) and (III), (I) is a catalyst for the hydrogenation and isomerization of olefins. Its catalytic behavior is similar in some ways to the other two isomers, but (I) gives faster rates for hydrogenation, in general, and is notably more stable than (II) and (III) under catalytic conditions.

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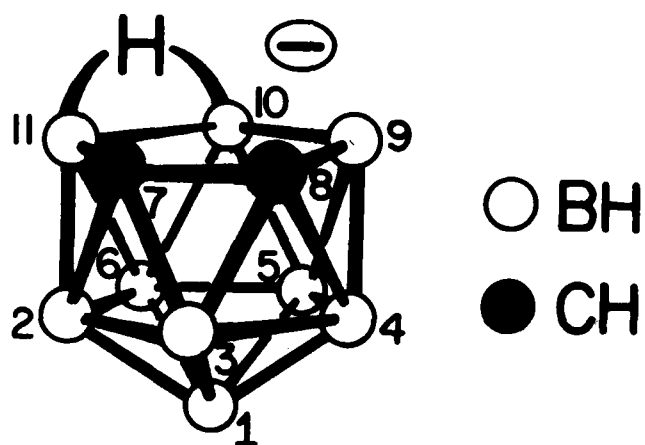


Figure 1.

The structure of the nido carborane anion,  
 $[7,8-C_2B_9H_{12}]^-$ .

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